Memorandum Report 1166

CORROSION MECHANISMS IN STEAM POWER GENERATION - A PROGRESS REPORT

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CONTENTS

ABSTRACT

A summary of conclusions reached in a basic research program concerned with the corrosion of steel under conditions encountered in steam power generation is given and the work done during the past year is described. This work has been concerned with

(1) The effect of OH^- concentration and of $OH^-/PO_4^{\equiv}$ ratios on corrosion rates and on the buildup and breakdown of protective films at 600°F

(2) The effect of non-adherent corrosion products on the development of localized attack at 600°F and

(3) The stabilization of protective films against breakdown upon exposure to air-saturated water at room temperature.

The studies revealed that the data of Berl and van Taack, upon which conclusions regarding the beneficial effects of NaOH additions to boiler water have been based, do not give an adequate picture of these effects. Increasing the pH in static systems at 600°F increases the corrosion rate. The size of the crystallites in the protective film also increases with pH and this may account for increased stability of the high pH films in high velocity streams. Concentrated NaOH at 600°F causes drastic pitting similar in appearance to that reported by British workers as characteristic of failed high pressure boiler tubes. The attack of steel by concentrated Na_2HPO_4 at 600°F is different in character than the attack by NaOH and it does not cause the drastic pitting characteristic of NaOH. Some protection against this drastic pitting is obtained in solutions with mol ratios of NaOH to Na_2HPO_4 as high as 3 to 1. Concentrated LiOH does not produce this drastic pitting.

The presence of non-adherent corrosion products results in drastic localized attack in highly oxygenated static systems at 600°F but seems to have little effect in the absence of oxygen.

Protective films having improved resistance to room temperature attack by air-saturated water may be obtained by operation at 600°F in an LiOH solution at a pH of 13.

The mechanisms responsible for the above-described phenomena are under investigation.

PROBLEM STATUS

This is a progress report. The work is continuing.

AUTHORIZATION

NRL PROBLEM NUMBER M04-01

PROJECT NUMBERS SR 007-08-08-0613, RR 007-08-44

INTRODUCTION

It has previously been concluded (1,2) that of the seven corrosion products which may be generated under boiler operating conditions, ($Fe(OH)_2$, Fe_3O_4, α- and γ-Fe_2O_3 and α-, β- and γ-FeOOH) only those having the spinel structure (Fe_3O_4 and γ-Fe_2O_3) are capable of forming adherent protective films and that the major problems of boiler operation are concerned with the genesis and breakdown of these protective films. It has been found that in the absence of oxygen, films of Fe_3O_4 form readily at comparatively low temperature and that at 600°F these films rapidly reduce the corrosion rate to practically insignificant values - of the order of a tenth of a mil per year at the end of a month of exposure.

The work of others (3) has demonstrated that the reaction rate with pure water continues to be low up to a temperature in the neighborhood of 1060°F at which temperature the spinel film is no longer stable. Instead, films of FeO are obtained and these films are not very protective. Under these conditions, therefore, alloys which stabilize the spinel film to higher temperature must be used. In fact, before this temperature is reached, mild steel becomes impractical to use due to the formation of CH_4 by attack of Fe_3C by corrosion-generated hydrogen, and alloys which contain carbides resistant to this breakdown must be employed. The precise temperature at which this breakdown becomes important remains to be determined.

In considering reactions at boiler operating temperatures in the 600°F region (1200 lb. boilers), the effects of additions to the water of OH^-, $PO_4^{\equiv}$ and Cl^- were investigated, and it was found that these additions had comparatively little effect when used in the concentrations normally encountered, upon corrosion rates at operating temperatures, and in the absence of oxygen.

Addition of oxygen to the boiler water, after formation of a protective film by operation for some time in its absence, did not produce pits in a 20-day operation, but if the oxygen was added at room temperature to a system containing both bare and protected metal, pits developed on the bare metal portion, reaching a depth of about 1 mil in 20 days.

1

Investigation of the effect of room-temperature exposure of protective films such as would be encountered during shutdown periods indicated that the Fe_3O_4 films, which were protective at elevated temperatures, could not withstand attack by air-saturated water at room temperature. It was shown that Cl^- is a very active promoter of film breakdown by air-saturated water, that OH^- and $PO_4^{\equiv}$ are protective, and that proper quantities of OH^- and $PO_4^{\equiv}$ will protect steel during long exposure to air-saturated water even in the presence of substantial amounts of Cl^-. It was pointed out (2) that breakdown of the protective films by exposure to air-saturated water at room temperature results in the genesis of FeOOH, a non-adherent corrosion product. Thus, this breakdown of protective films by air exposure during shut down periods not only may be the cause of pit formation per se, but also may be the cause of the genesis of much non-adherent material. It was pointed out that if this material were not removed prior to the resumption of operations, it might deposit at unfavorable locations and act as a barrier to heat transfer and to diffusion of solution or of dissolved species to and from the metal-solution interface. The barrier to heat transfer would produce a hot spot and a thermogalvanic cell, the barrier to diffusion a concentration cell.

Previously (1) a detailed investigation of the effect of alkali had been started. Particular attention was directed to possible deleterious effects produced by high alkali concentrations which might result from high steaming rates or other causes. In addition to its intrinsic interest, it was known from previous experience that such concentration could produce trouble and there was particular concern regarding the exact nature of this trouble in terms of basic mechanisms of film breakdown. Caustic had been associated with embrittlement and there was some suspicion that it might be related to pitting as well. Experiments with 40% NaOH in capsule systems gave conclusive proof that caustic concentration can be responsible for pitting and that the pits thus generated are remarkably similar to those reported by the British as typical of what they find in their high-pressure boilers. Fig. 1 shows corrosion rates obtained by the hydrogen effusion technique (4) for three representative capsules containing 40% sodium hydroxide solution together with rate data from a water-filled capsule. When the capsules were opened after the experiment it was found that pitting attack had occurred near
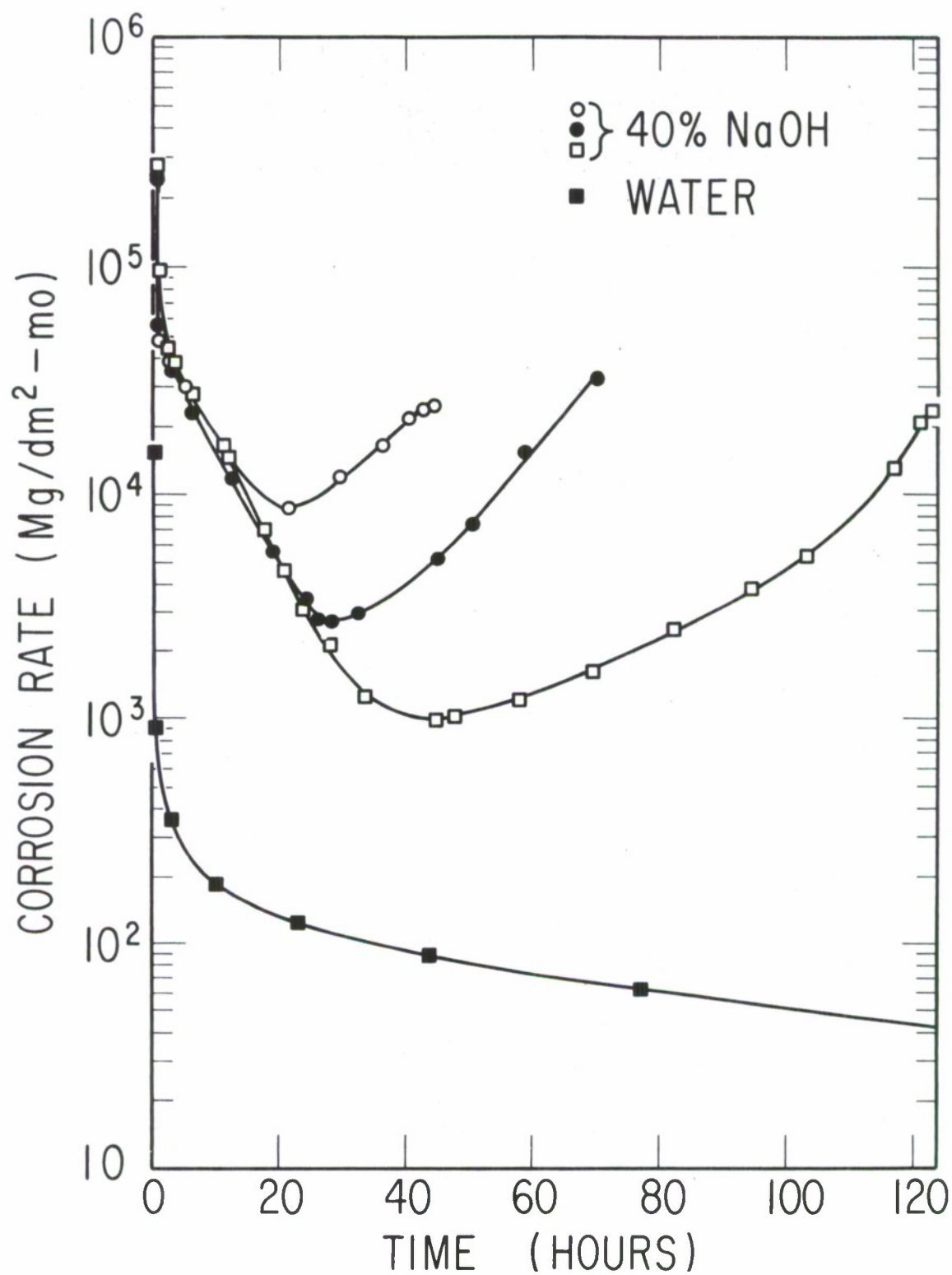
2

Fig. 1 - Corrosion rates of mild steel capsules containing water or 40% sodium hydroxide solution at 316°C

the ends of the capsules. During spot welding
of the capsules martensite is formed at the capsule
ends and the pitting attack occurred at the martensite-
ferrite boundary or in the ferrite near the boundary,
a region which was subjected to plastic deformation
during fabrication and subsequent heating. The onset
of the pitting attack coincided approximately with
the end of the decrease in hydrogen effusion rates
and the beginning of the rate increase. Figure 2
shows a section through one end of a capsule that was
filled with 40% sodium hydroxide solution and removed
from the oven after 24 hours, at a time when the rate
was still decreasing.

This capsule, and also those shown in Figs. 3, 4
and 5, was silver-plated to provide a backing for
holding the corrosion product in place during preparation
for metallographic examination. The weld is at the
left in Fig. 2, and the martensite, showing as the dark
areas, is plainly visible. Although the catastrophic
preferential attack has not yet begun in this capsule
after 24 hours, it is readily seen in the 46-hour
sample (Fig. 3), at which time the corrosion rate was
increasing. The preferentially attacked sites on
opposite walls of the capsule are plainly visible; pits
were filled with corrosion product. Numerous pits
developed in the vicinity of the martensite-ferrite
boundary, so that grooves approximately perpendicular
to the plane of Fig. 3 were formed.

Figure 4 shows one of the pits of Fig. 3 at
higher magnification. The catastrophic attack seems
to start at a point and proceed in all directions at
approximately the same rate so that individual pits
are approximately hemispheric in shape.

Figure 5 shows a section through opposite walls
of a capsule near a welded end. The capsule wall at
the bottom has been perforated, and the wall at the
top is nearly perforated. The pits have smooth
surfaces, the pitting attack showing no preference
for grain boundaries or other physical features of
the metal. This is in contrast to the general attack
over most of the capsule surface, an example of which
is shown in Fig. 6. Here the general corrosion
proceeds on an irregular front, possibly showing some
preference for grain boundaries. Magnetite was the
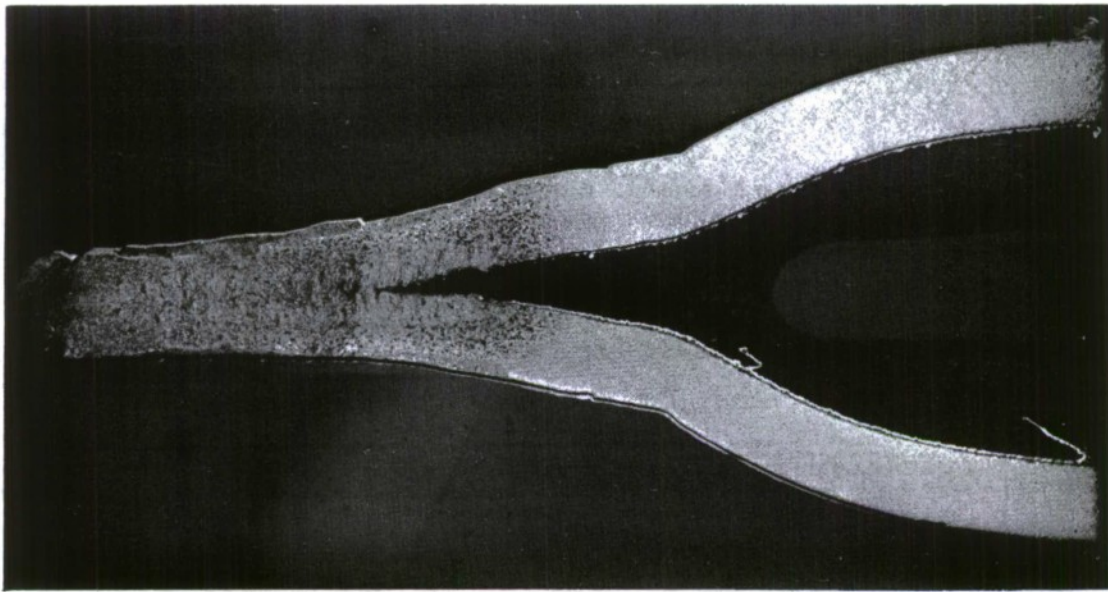only corrosion product found.

4

Fig. 2 - Section through end of mild steel capsule that was filled with 40% sodium hydroxide solution and t r e a t e d at 316 °C (600 °F) for 24 hours. 1% Nital. Magnification: 15X. (Reduction in printing approximately 10%.)
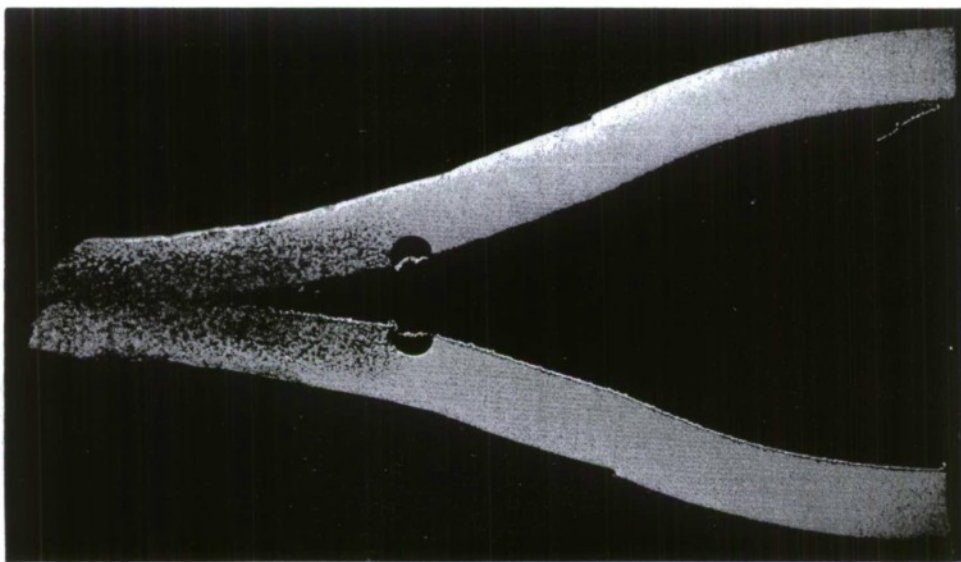

Fig. 3 - Section through end of mild steel capsule that was filled with 40% sodium hydroxide solution and t r e a t e d at 316 °C (600 °F) for 46 hours. 1% Nital. Magnification: 15X. (Reduction in printing approximately 10%.)

Fig. 4 - Magnified view of one of the pits shown in Fig. 3. 1% Nital. Magnification: 200X. (Reduction in printing approximately 35%.)
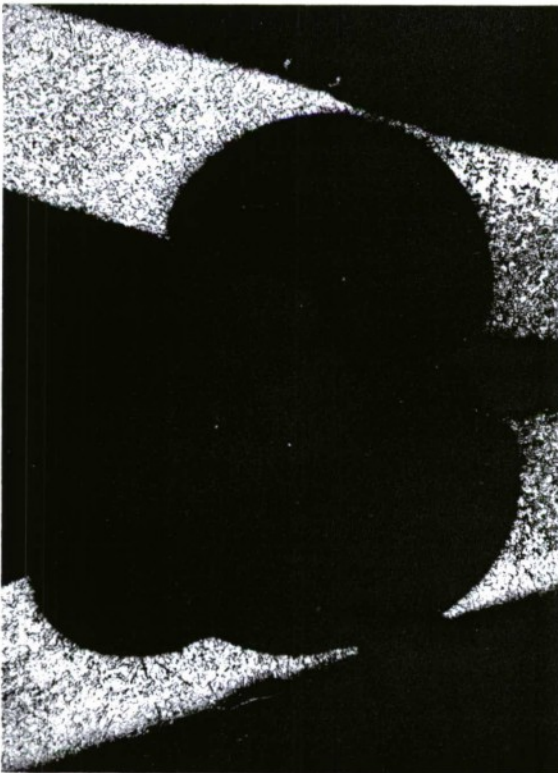
Fig. 5 - Section near end of mild steel capsule that was filled with 40% sodium hydroxide solution. The capsule leaked after 51.6 hours at 316°C (600°F) and was immediately removed from the oven. 1% Nital. Magnification: 50X. (Reduction in printing approximately 35%.)

Fig. 6 - Section through inside surface of same capsule shown in Figs. 3 and 4 showing appearance of general corrosion over most of capsule surface. 1% Nital. Magnification: 200X. (Reduction in printing approximately 8%.)

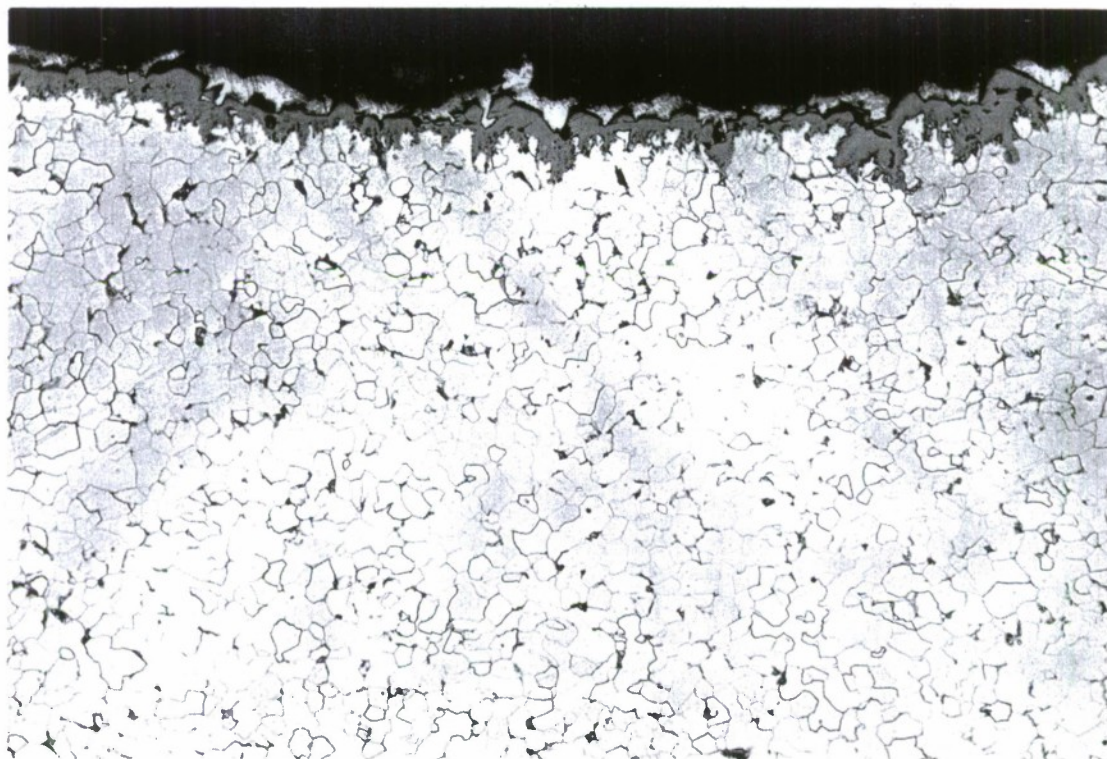Figure 7 shows a typical pattern of the pitting observed in British high-pressure boilers (5). There is a striking similarity between this and Fig. 5.

One phase of the program during the current year has been directed toward understanding the effect of caustic concentration upon corrosion rates and upon the buildup and breakdown of protective films, another phase being concerned with the effect of non-adherent corrosion products and with attempts to stabilize the protective film so that such products will not be generated.

EFFECTS OF CAUSTIC CONCENTRATION

The overall picture of corrosion rates in caustic solutions which has thus far been obtained is shown in Fig. 8.

Since these data lead to conclusions contrary to those of Berl and van Taack (6), which have been the main basis for the use of NaOH in boiler operation over the years, a detailed investigation of effects in the region of low caustic concentration, the region of the disagreement and of normal boiler operation, has been made. The data are not yet quite complete but enough has been done to show the general outlines of the work (Table 1).

It may be observed that while the NRL data show a continuous increase in the total corrosion at the end of 7½ hours as the pH increases from 7 to 12, they do confirm the drop in total corrosion reported by Berl and van Taack in the pH region of 12.2. These data indicate, however, that this advantage is a temporary one and that the corrosion rate after 25 days increases with pH.

Some partial answers regarding what is happening to the protective film to cause these changes are indicated in Figs. 9-11. It may be noted that increase in pH is accompanied by a marked increase in the size of the crystals in the protective films. Thus, the surfaces of the films generated at pH of 10.6 and 11.5 show the sharp linear outline of cross sections of crystal faces whereas the surface of the film generated at a pH of 7 does not. The x-ray patterns obtained from the films generated at a pH of 7 showed line broadening, indicating that the major mass of this deposit has a crystallite size less than 1000 A. It
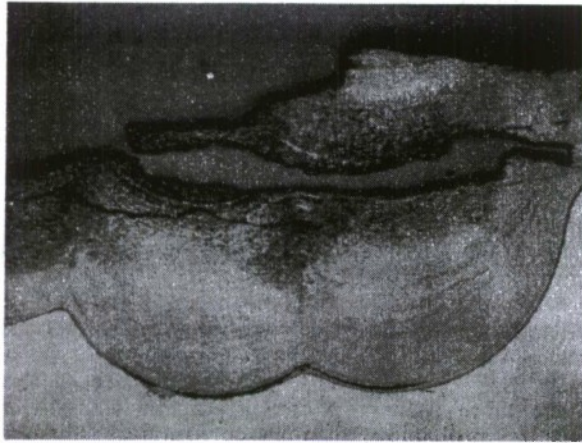
8

Fig. 7 - Section through pit showing
metal/magnetic oxide interface.
Magnification: 10X. (From Ref. 5.)

Fig. 8 - Corrosion rate of mild steel at 316°C (600°F).
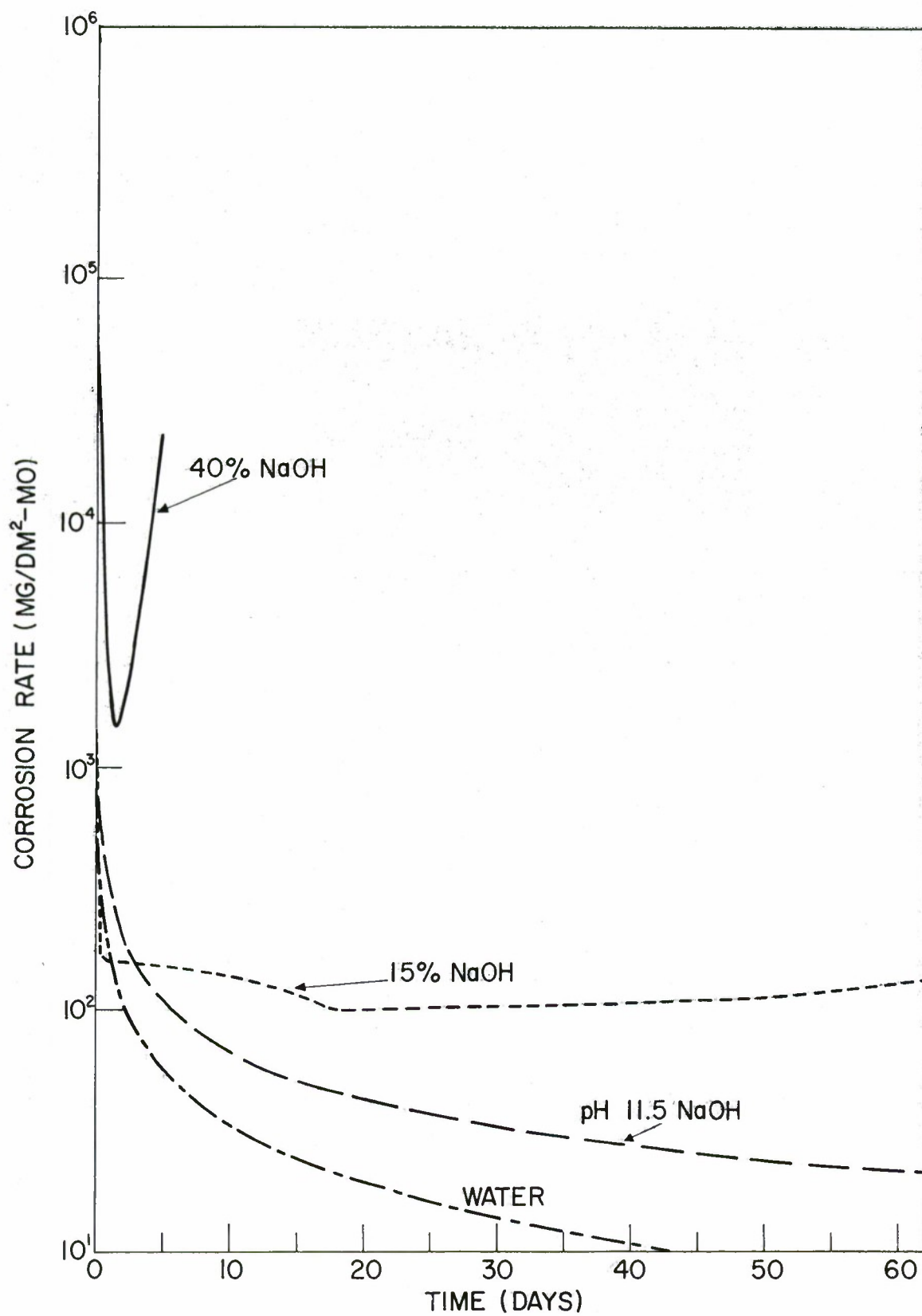
The figure shows corrosion rate (MG/DM²-MO) on the vertical logarithmic axis (from 10^1 to 10^6) versus time (days) on the horizontal axis (0 to 60). Curves are labeled: 40% NaOH, 15% NaOH, pH 11.5 NaOH, and WATER.

TABLE 1

Corrosion of Mild Steel by
Solutions of NaOH at 310° to 316°C

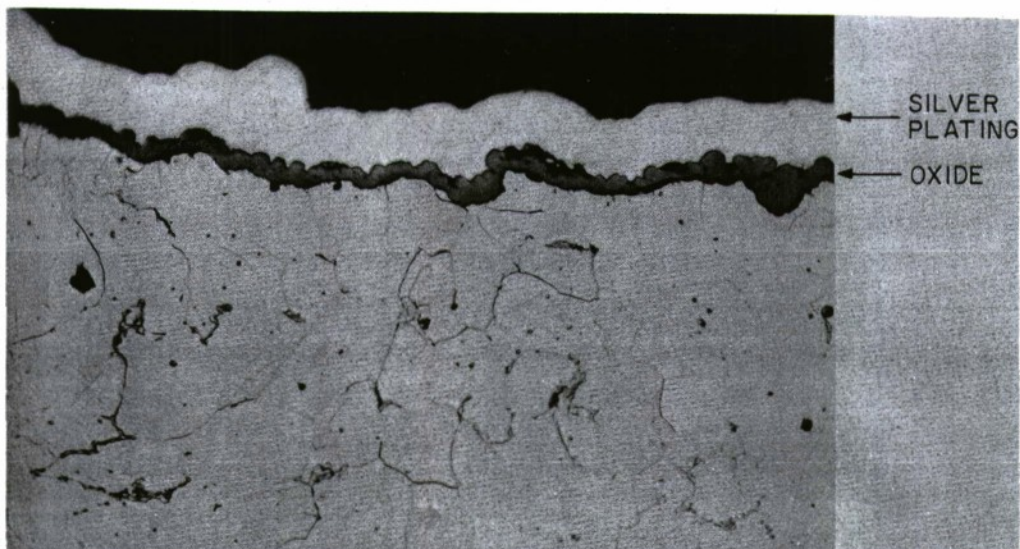| pH	Total Corrosion After 7.5 Hours		Corrosion Rate at 316°C ($mgFe/dm^2$-mo)	
	Berl and (310°C) van Taack	NRL (316°C)	After 7.5 Hours	After 25 Days
	$(mgFe/gFe)$	$(mgFe/dm^2)$		
7.00	45	7	330	16
10.6		10	580	22
11.5		11	680	37
11.70	42			
12.00	42	23	970	52
12.18	29			
12.24		5	220	55
12.32	29			
12.40	47			

11

Fig. 9 - Section perpendicular to inside surface of mild steel capsule that was filled with water and treated at 316°C (600°F) for 789 days. Sample silver-plated before polishing. 1% Nital. Magnification: 1000X. (Reduction in printing approximately 35%.)

Fig. 10 - Section perpendicular to inside surface of mild steel capsule that was filled with pH 10.6 sodium hydroxide solution and treated at 316°C (600°F) for 439 days. Sample silver-plated before polishing. 1% Nital. Magnification: 1000X. (Reduction in printing approximately 35%.)

12

Fig. 11 - Section perpendicular to inside surface of mild steel capsule that was filled with pH 11.5 sodium hydroxide solution and treated at 316°C (600°F) for 283 days. Sample silver-plated before polishing. 1% Nital. Magnification: 1000X. (Reduction in printing approximately 35%.)
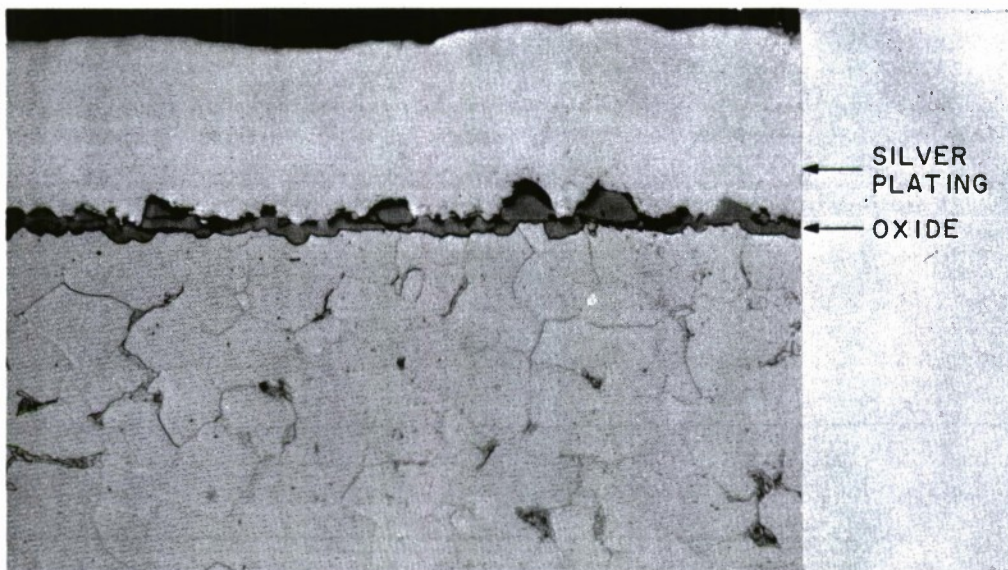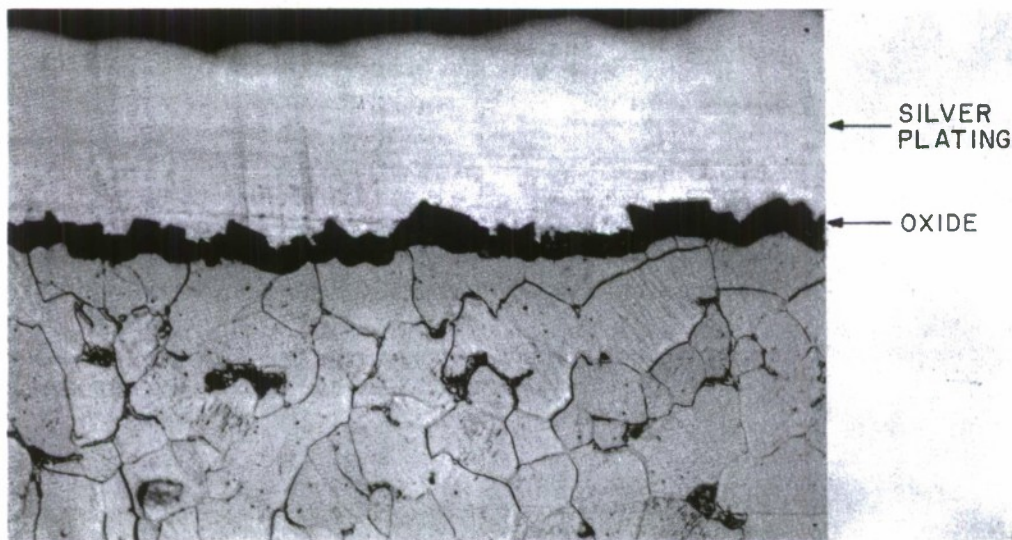
13

may be significant in this connection to mention that
experiments in loops at high velocity (7) have indicated
that alkalization to a pH of 10 to 12 has a beneficial
effect on long-time operation. It would appear that
this difference may be due to the colloidal particle
size of the deposits generated in low pH water which
causes these deposits to go into colloidal solution
in high-velocity streams.

In the case of the 40% NaOH it appears that a
thick adherent continuous film of Fe_3O_4 is generated
rapidly (Fig. 6) with much grain boundary penetration.
Fe_3O_4 films are very good electronic conductors, and
break down at some "weak spot" which exposes the
unprotected steel is a favorable condition for pit
development. The exposed spot constitutes a small
anode, and the whole surface of the conductive Fe_3O_4
is available as a cathode in a highly conductive
solution. Why it takes these high concentrations of
caustic to cause breakdown at "weak spots" and what
constitutes a "weak spot" is yet to be fully established.
Present indications point to weld-heat-affected zones
as one such spot.

Specimens corroded in 15% NaOH have not yet
been examined microscopically. The significance of
the upward trend in the corrosion rate after 20 days
which is shown in Fig. 8 is not yet clear. It may
be a concentration effect since water is used up in
the reaction

$$3Fe \quad + \quad 4H_2O \rightarrow Fe_3O_4 \quad + \quad 4H_2.$$

A clear picture of why increasing alkalinity
causes an increased corrosion rate has not yet been
obtained. Clearly, if the films are tight and water
cannot penetrate, the mechanism of attack must involve
outflow of Fe ions from the metal and inflow of H^+
from the solution through the film. Why the presence
of more OH^- in the water should affect the rates of
these processes is not clear. Perhaps OH^- gets into
the film and opens it up by producing cation vacancies
as suggested by Douglas (8). Perhaps the reaction
at the oxide/solution interface where Fe ions leave
the film to form additional Fe_3O_4 by reaction with OH^-
from the solution controls the rate of these processes,
and OH^- accelerates this. Currently, attempts are
being made to find out by infrared analysis whether
OH^- is incorporated in the film.

In connection with caustic attack, the question
of its mitigation by the use of proper $OH^-/PO_4^{\equiv}$ ratios
is one which seems to call for analysis. Despite the

wide use of this technique, the reasons for its
effectiveness have apparently not been investigated.
The Purcell - Whirl thesis (9) on which this is based
calls for maintaining an $OH^-/PO_4^{\equiv}$ ratio equivalent to
the use of Na_3PO_4, i.e., in terms of NaOH and Na_2HPO_4,
a one-to-one ratio,

$$NaOH \quad + \quad Na_2HPO_4 \longrightarrow Na_3PO_4 \quad + \quad H_2O,$$

but says nothing about deviations from this ratio.
Some analyses of corrosion products associated with
a very considerable attack on piping on the USS EDWARDS (10)
seemed to point to the possibility of attack by
concentration of Na_2HPO_4 itself. One portion of the
program, therefore, has been devoted to an analysis
of these effects. Some of the progress made in this
connection is illustrated in Fig. 12 which shows
corrosion rates obtained in solutions containing
varying $NaOH/Na_2HPO_4$ ratios with approximately
40% solids. The pure NaOH curve starts at a very high
rate, decreases during the first day and a half, and
then increases again, rising to high values and leading
to pitting and perforation of the capsule wall within
a few days. The curve for pure Na_2HPO_4 shows a steady
decrease from the very high initial rate for about
17 days and then a steady rate for the next 13 days
after which the experiment was terminated. In the
curve for the 3:1 mol ratio of $NaOH/Na_2HPO_4$, we
note again an initial drop in rate followed by a recovery
and then a fluctuating but substantially constant rate
from 5 to 45 days followed by a continued fluctuation
but gradual rise for the next 15 days after which the
capsule was removed for examination.

Examination of the capsule ends indicates that
the drastic pitting attack produced by the pure caustic
solution has been avoided in both cases when phosphate
was present. Microscopic examination of the capsule
walls indicates, however, that the action of the
phosphate is apparently not one of preventing damage
to the magnetite film. Thus, Fig. 13 shows the film
generated on the surface of the steel in the case of
the 40% Na_2HPO_4. This film is very thin (2 microns or
less), much thinner than the magnetite film which would
be expected after this amount of corrosion had taken
place with formation of magnetite. Moreover, substantial
amounts of a crystalline red corrosion product were
obtained, probably a phosphate, which is currently
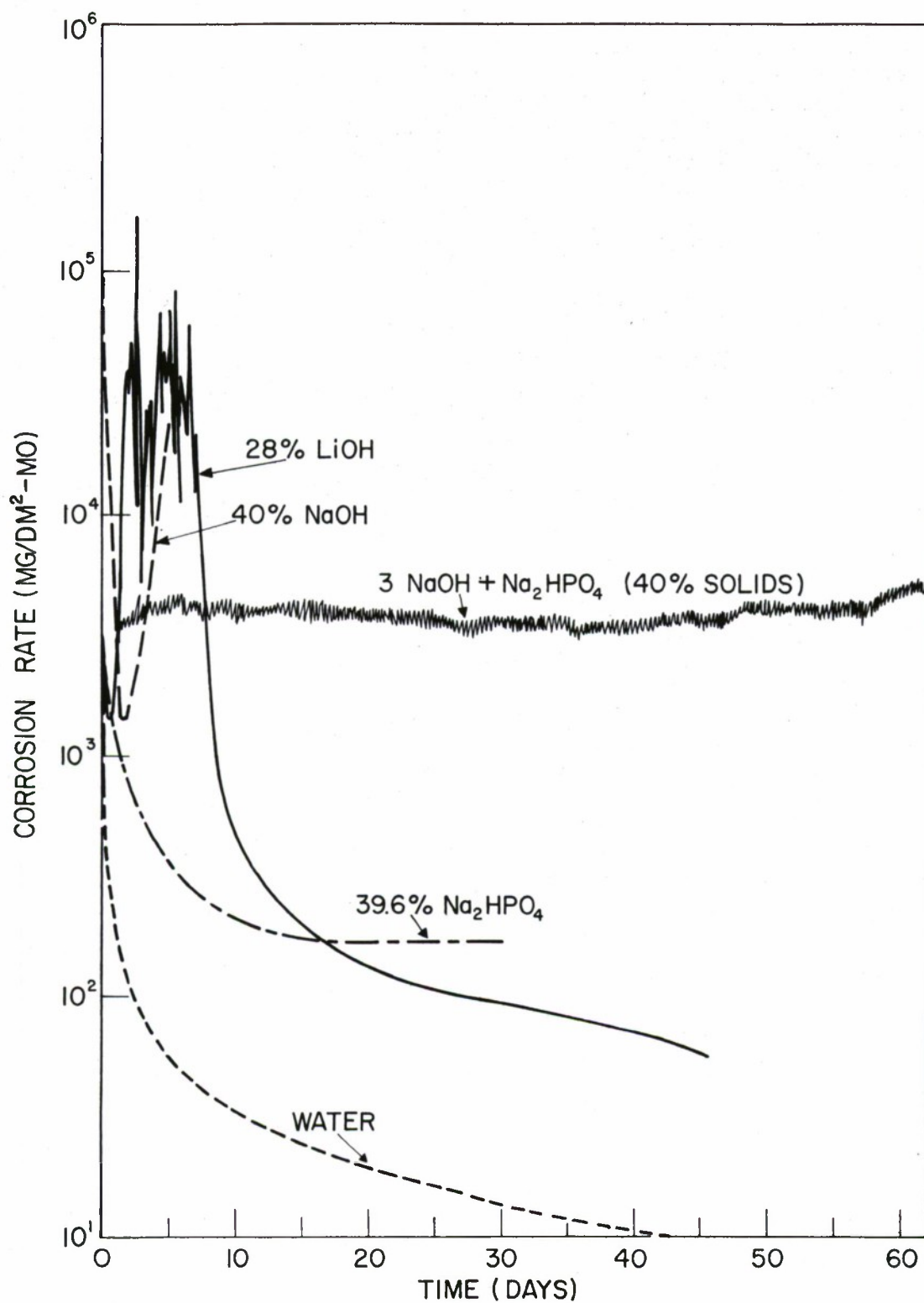being subjected to x-ray and chemical analyses.

15

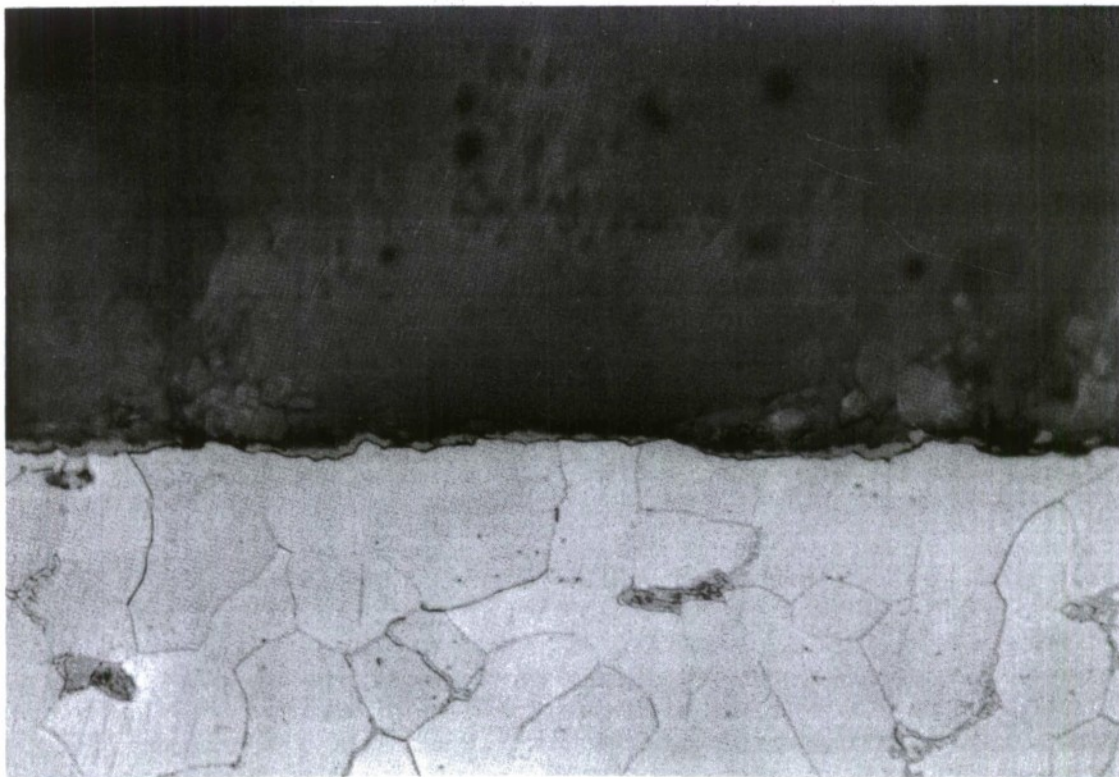Fig. 12 - Corrosion rate of mild steel at 316°C (600°F)

16

Fig. 13 - Section through inside surface of mild steel capsule filled with Na_2HPO_4. $12 H_2O$ and maintained at $316°C$ for 30 days. 1% Nital. Magnification: 1000X. (Reduction in printing approximately 8%.)

Figure 14 shows the corrosion product generated on the surface of a capsule filled with the solution containing hydroxide and phosphate in the 3:1 mol ratio of $NaOH/Na_2HPO_4$. The corrosion product was found to be soft and relatively nonadherent. Clearly the picture is not yet complete.

Since it has been demonstrated in the work carried on in connection with pressurized water reactors that LiOH as a water additive is effective in stabilization of the deposit to movement in high-velocity streams, and since in addition, LiOH is interesting theoretically in terms of the possible incorporation of Li directly into the spinel structure of Fe_3O_4, some experiments were performed in which the OH^- concentration was maintained by LiOH at the same level as in the 40% NaOH solutions. The data obtained in these experiments are exhibited in the curve marked 28% LiOH (Fig. 12). Again the initial drop in corrosion rates is followed by a rise to high values as in the case of the 40% caustic solution but in this case localized attack and penetration of the wall was not observed. Instead, after 10 days of operation at high rates, the rates started a continuous drop. Photomicrographs taken after 23 days at temperature show no signs of pitting attack. In this case we have evidence of why the LiOH acts differently from the NaOH.

Figure 15 shows the LiOH corrosion rate vs. time curve on an expanded scale. Samples removed within the first 12 hours, before the rate starts to rise, show, as we might expect, the normal Fe_3O_4 film whose presence is causing the rate to drop. If, however, a sample is removed after the start of the rise, it is found that a new corrosion product is starting to form and gradually replacing the Fe_3O_4. Analysis shows this new corrosion product to be $LiFeO_2$ and it is not adherent. It appears that this new solid phase must form by the reaction

$$Fe_3O_4 + 3LiOH \longrightarrow 3LiFeO_2 + H_2O + 1/2 H_2.$$

Thus some of the hydrogen which was evolved and used in calculating the corrosion-rate on the LiOH curve is associated not with corrosion but with this reaction. Secondly, and of greater import, it may be noticed that whereas the reaction which produces magnetite,

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2,$$

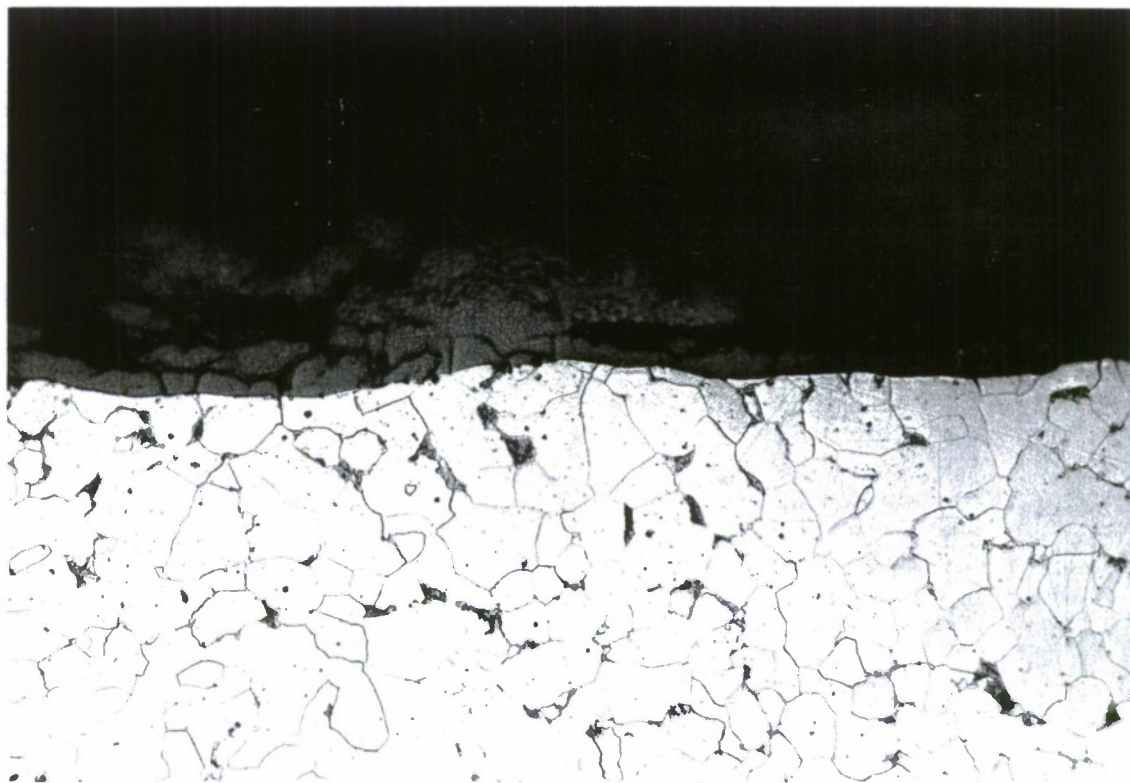consumes water and thus increases any OH^- concentration

Fig 14 - Section through inside surface of mild steel capsule filled with NaOH and Na_2HPO_4 in the mol ratio 3:1, total solids = 40%, and maintained at 316°C for 30 days. 1% Nital. Magnification: 1000X. (Reduction in printing approximately 8%.)
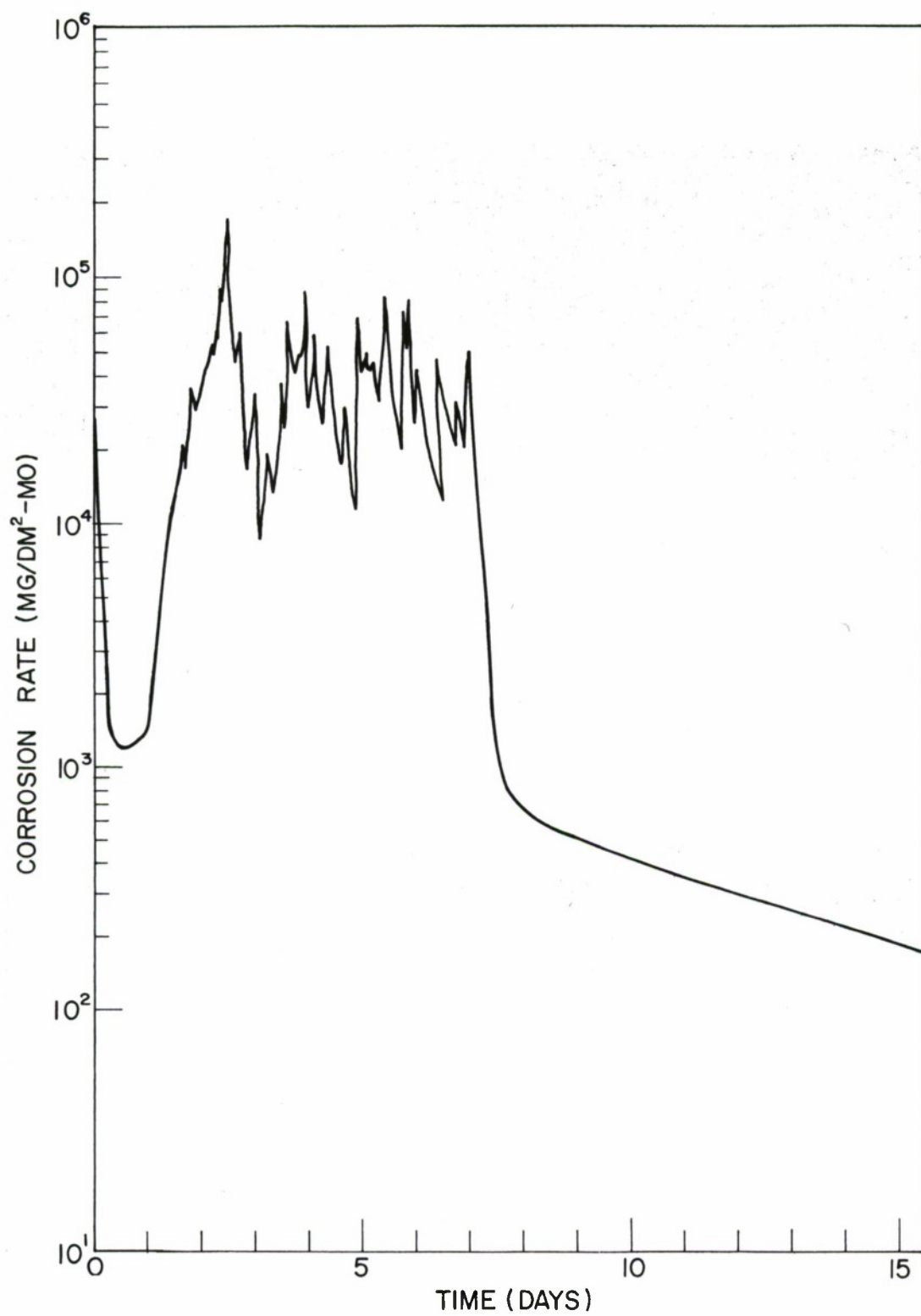
Fig. 15 - Corrosion rate of mild steel in 28% LiOH
at 316°C (600°F)

20

originally present, the reaction which produces the $LiFeO_2$ consumes OH^- and generates H_2O thus continually diluting the OH^- concentration. This would appear to explain the oscillations of the corrosion rate curve, which is a function of H_2 generation. If one postulates, and there are good reasons for this, that the transformation of Fe_3O_4 to $LiFeO_2$ takes place at a certain specific OH^- concentration, then one can see the reason for the oscillations, for as soon as some Fe_3O_4 is converted to $LiFeO_2$, some OH^- is consumed in the immediate vicinity of the deposit and more Fe_3O_4 begins to form. As time passes, however, more OH^- diffuses in from the bulk solution and the process is repeated. The $LiFeO_2$ is nonadherent and the reaction proceeds throughout the capsule giving a general corrosion instead of the concentrated catastrophic pitting which is effected by concentration of the NaOH in the neighborhood of massive Fe_3O_4. That the use of LiOH in place of NaOH may give protection against this type of pitting without the need of phosphate or other addition is one item which requires further investigation. The need for carrying this work further is obvious.

PROTECTIVE FILM FAILURE AND THE EFFECTS OF NONADHERENT
  CORROSION PRODUCTS.

The second phase of the research program takes off from the previous conclusions that a major source of trouble is the failure of the protective film as a result of room temperature exposure to air-saturated water during shutdown periods and the resultant generation of nonadherent corrosion products. These products would be transported in the flowing stream during boiler operation and might deposit at some unfavorable spot where they could build up insulating films and act as a barrier to diffusion and heat transfer. As noted in the introduction to this report, the attack on this problem has been a twofold one. In the first place, investigation is being made of the effect on test specimens of deliberately introducing corrosion products at specific locations prior to exposure of the test specimens to oxygenated as well as non-oxygenated solutions. In the second place, investigation is being made of the possibility that the protective film might be stabilized against room-temperature attack by air-saturated water by incorporating in the film other substituents introduced either from the water or from the metal.

21

A simple, cheap, reusable form of autoclave has been developed for work at 600°F in both areas of study. The body of the autoclave consists of drilled-out cold-rolled steel rod, and the closure is a capped Ermeto union, readily available commercially. Both ½-in. and 1-in. O.D. autoclaves of this type have been used successfully.

EFFECTS OF NONADHERENT CORROSION PRODUCTS

In this work a series of experiments was performed in which mild steel covered with masses of corrosion product at localized areas was subjected to corrosion in aqueous solutions at 600°F. The specimens were disks of mild steel in one face of which a small cavity 1/16-in. deep and 0.076-in. in diameter was drilled. Each cavity was filled to about one half of its depth with one of the following corrosion products of iron: γ-FeOOH, Fe_3O_4, or α-Fe_2O_3. The cavities served the purpose of defining the areas of the specimen in contact with overlying corrosion products and of retaining these products in place during subsequent treatment. Similar specimens, cavity-side up and three to a holder, were placed in separate clean steel autoclaves. One of the following solutions was added to each autoclave: distilled water, 0.001 molar NaOH solution, 4% hydrogen peroxide solution. The hydrogen peroxide decomposes to form water and oxygen and therefore served as a convenient method of providing an oxygenated water solution.

The specimens, removed after 4 weeks exposure at 600°F were silver-plated to retain corrosion products, sectioned, polished, and examined. Microscopic examination of these polished sections gave the results shown in Table 2.

Figure 16 shows representative areas both outside and inside the cavities of specimens in which there is no evidence of accelerated corrosion attack within the cavity.

Figure 17 shows representative areas of specimens in which corrosive attack has definitely been greatly accelerated within the cavity and again shows areas both outside and inside the cavity.

Characteristic of the first type of specimen are the visible traces of cold working during the drilling operation in Fig. 16b and the absence of such traces in

22

TABLE 2

The Effect of Overlying Corrosion Products (γ-FeOOH, Fe_3O_4, and α-Fe_2O_3) in Accelerating Corrosive Attack on Steel Specimens at 600°F in H_2O, 0.001N NaOH and 4% H_2O_2 Solutions. (Time of 600°F Exposure = 4 Weeks in Each Case.)

| Material Placed in Drilled Cavity	Solutions Used	Remarks
γ-FeOOH	Distilled H_2O	Thin adherent oxide film both inside and outside cavity. No evidence of accelerated corrosive attack in cavity.
Fe_3O_4	Distilled H_2O	"
α-Fe_2O_3	Distilled H_2O	"
γ-FeOOH	0.001N NaOH	"
Fe_3O_4	0.001N NaOH	"
α-Fe_2O_3	0.001N NaOH	"
γ-FeOOH	4% H_2O_2	Outside cavity - thin adherent oxide film. Inside cavity - many areas of heavily accelerated corrosive attack, both transgranular and intergranular.
Fe_3O_4	4% H_2O_2	"
α-Fe_2O_3	4% H_2O_2	"
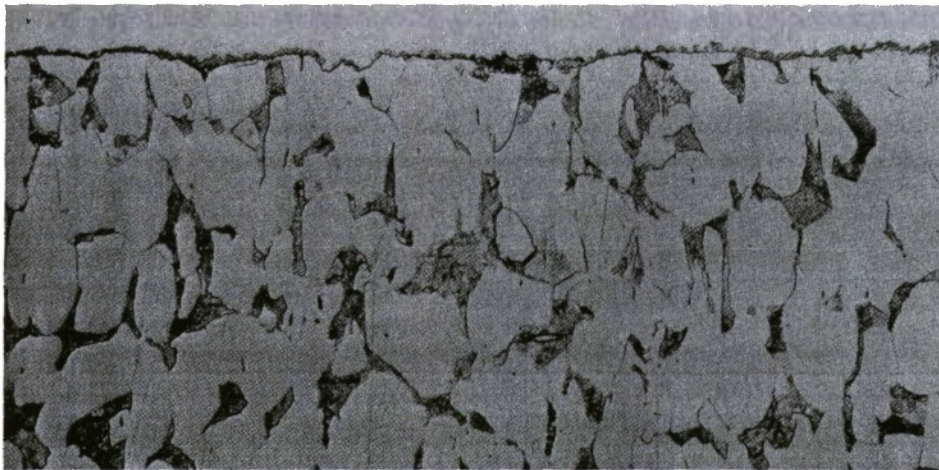
Fig. 16a - Section through bare steel area remote from cavity in specimen exposed to 600°F distilled water. Original magnification: 500X. (Reduction in printing approximately 20%.)
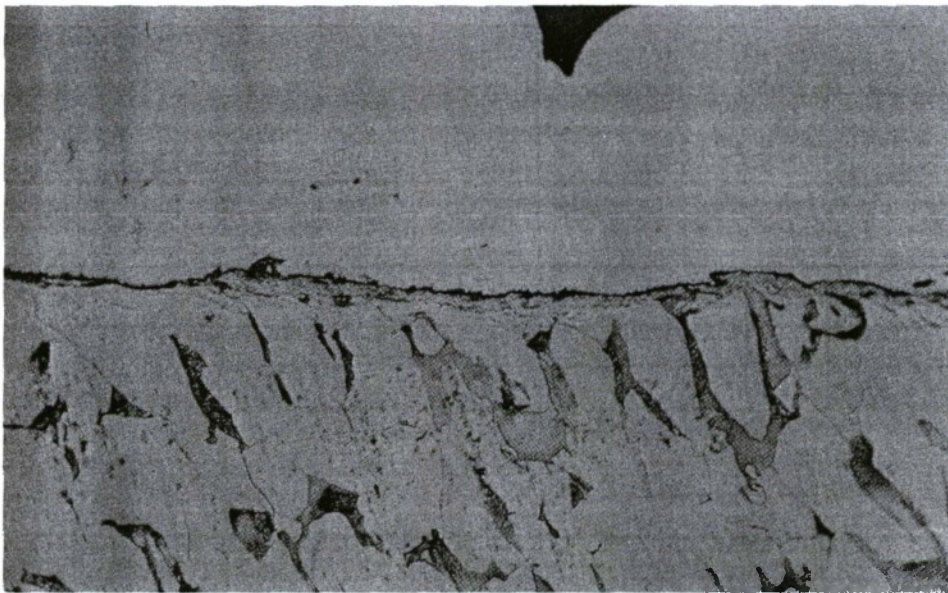

Fig. 16b - Section through area within the Fe_3O_4 filled cavity in the specimen in Fig. 16a. Original magnification: 500X. (Reduction in printing approximately 20%.)

Fig. 17a - Section of bare steel area remote from the cavity in specimen exposed to 600°F, 4% H_2O_2 for 4 weeks. Original magnification: 500X. (Reduction in printing approximately 20%.)
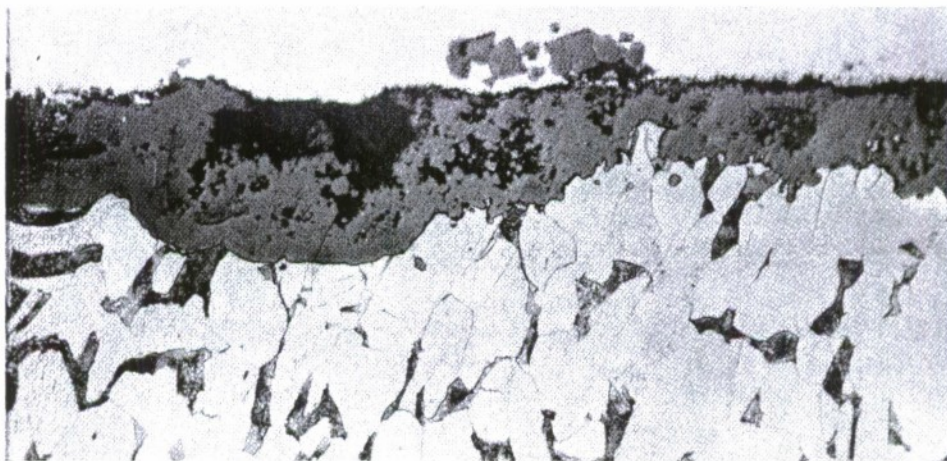

Fig. 17b - Section through area within the Fe_3O_4 filled cavity in the specimen in Fig. 17a. Original magnification: 500X. (Reduction in printing approximately 20%.)

Fig. 17b, where the accelerated corrosion has destroyed the metal of the original cold-worked surface.

These experiments indicate that the presence of corrosion products on a steel surface in contact with aqueous solutions at $600^{\circ}F$ has little effect upon corrosive attack of the underlying steel in the absence of oxygen but may have a profound effect in the local acceleration of attack beneath these deposits in the presence of oxygen. This would indicate an oxygen concentration cell as the mechanism for the accelerated attack.

STABILIZATION OF THE PROTECTIVE FILM

One of the guide lines in the studies on stabilization of protective spinel films on steel has been the possibility of incorporating substituent cations in the spinel (Fe_3O_4 or γ-Fe_2O_3) structure, since it is known that such substitution will greatly affect the resultant properties of the material. In initial studies small specimens of mild steel were exposed four weeks in autoclaves at $600^{\circ}F$ to distilled water and to solutions containing various cations (Na^+, Li^+, Zn^{++}, Mg^{++}, Al^{+++}, Cu^{++}, Ca^{++}) in 0.1 or 0.01 molar ion concentrations, as NaOH, LiOH, $ZnSO_4$, $MgSO_4$, $Al_2(SO_4)_3$, $CuSO_4$, $Ca(NO_3)_2$, the anions used being determined primarily by their known or inferred lack of deleterious effect on the stability of spinel films and sufficient solubility of the selected cation-anion combinations. Stability of the spinel films which were formed on these specimens by elevated temperature corrosion was checked by exposure of the filmed specimens to air-saturated distilled water at room temperature for periods up to two weeks.

Visual observations of breakdown indicated that the spinel films formed in the LiOH and $CuSO_4$ solutions were definitely more resistant to room-temperature deterioration than those formed in water. The films formed from $Ca(NO_3)_2$ solution and possibly also the NaOH solution appeared more stable than those formed in pure water, and while lower concentrations of $Al_2(SO_4)_3$, as well as 0.1 molar $MgSO_4$ and $ZnSO_4$ showed no evidence of increased stability of the film, some increased stability was shown by films formed from more concentrated $Al_2(SO_4)_3$ solution (Al^{+++}=0.1 molar). However, reproducibility was rather poor in the entire series of experiments so that conclusions from them are only tentative.

To overcome the problem of poor reproducibility, a holder was devised capable of supporting freely eight specimens simultaneously during 600°F exposure. The holder was so constructed that removal of specimens and transfer to the room-temperature-exposure vessel could be made with forceps touching only one area of the specimen. This area was then dropped into a hole in a Teflon holder and embedded in paraffin to isolate it from the test solutions.

A series of spinel-filmed specimens was then prepared by treatment of similar steel samples for four weeks at 600°F in distilled water and 0.1 molar cation solutions of $ZnSO_4$, Li_2SO_4, $Al_2(SO_4)_3$, $MgSO_4$, NaOH, and LiOH. In addition, spinel-filmed specimens of copper-plated and of zinc-plated steel were prepared by similar treatment in distilled water at 600°F.

Exposure of these coated specimens to air-saturated water at room temperature produced rapid attack on the copper-plated and zinc-plated specimens. After a two-week exposure, no sign of corrosion was observed on the LiOH and NaOH specimens, very little on the water-formed specimen, and varying amounts on the specimens formed in $Al_2(SO_4)_3$, $ZnSO_4$, and $MgSO_4$ solutions. The exposure history of these specimens was still not very satisfactory for comparative conclusions, however, because of poor reproducibility. Furthermore, all specimens were only lightly attacked including the water-formed ones, excluding only the copper and zinc plated specimens which had a heavy attack.

To develop a better criterion for comparative conclusions, it was essential to increase the severity of the attack so that water-formed specimens would definitely break down and the absence of breakdown would then clearly indicate stabilization. Water-formed and 0.1 molar LiOH-formed Fe_3O_4 films on steel were chosen as the best established examples of films between which differentiation must be made and some 40 specimens of each type were prepared by 600°F treatment for 6 weeks in the two media. For this purpose the severity of attack of the test fluid was increased by dissolving various low concentrations of NaCl in the distilled water.

The data of Table 3, obtained by using Teflon holders for triplicate exposure at room temperature, show conclusively that films developed by 600°F treatment in 0.1 molar LiOH are more resistant to

27

TABLE 3.

Number of Specimens Showing Corrosion (out of 3 exposed) After Room-temperature Exposure to Various Air-saturated Solutions for Various Periods

Corrosion Solutions	1 DAY		3 DAYS		5 DAYS		6 DAYS		15 DAYS	
	Formed in LiOH	Formed in H_2O	Formed in LiOH	Formed in H_2O	Formed in LiOH	Formed in H_2O	Formed in LiOH	Formed in H_2O	Formed in LiOH	Formed in H_2O
H_2O	0	1	--	--	0	1	--	--	0	3
1 ppm Cl^-	0	1	0	1	--	--	0	3	--	--
2 ppm Cl^-	0	2	--	--	0	3	--	--	0	3
3 ppm Cl^-	0	2	0	2	--	--	0	2	--	--
6 ppm Cl^-	0	2	0	3	--	--	1	3	--	--
9 ppm Cl^-	1	3	1	3	--	--	3	3	--	--
10 ppm Cl^-	0	2	--	--	2	3	--	--	2	3

Note: Dashes indicate that no specimens were examined.

28

room-temperature deterioration than films developed by analogous treatment in distilled water. These data further indicate that exposure in triplicate to aqueous solutions containing 4 to 5 ppm of chloride for several days is a satisfactory test for relative stability of the spinel film.

Metallographic examination of both types of specimens (after silver plating to retain the spinel film in place during cutting and polishing) shows clearly that one of the major differences between the two is the thicker and relatively more uniform nature of the spinel film formed on the LiOH-treated steel (Figs. 18 & 19). The oxide in the water-formed film appears to be a peculiar combination of a very thin continuous film overlaid by much thicker "blobs" or "boulders", the thickness of the latter being of the same order of magnitude as that of the film formed on the LiOH-treated steel. Solution of the spinel film in hydrochloric acid and flame spectrophotometry of the resultant solution has shown that the film formed by the LiOH treatment contains somewhat more than 0.4 atomic percent $\left(\dfrac{Li}{Li + Fe} \times 100\right)$ of lithium.

FUTURE WORK

In connection with the investigation of the effects of alkalization, the immediate program calls for further study of the mechanism of caustic attack, of the effects of lithium hydroxide and of the protective effect of phosphates.

In connection with nonadherent corrosion products, additional experiments are now proceeding in which the effects of varying the oxygen concentration and the length of time of exposure to elevated temperature attack are being explored. These experiments include blank runs with no packing in the cavities. Other specimens are being run under similar conditions with copper powder packing and copper plating to check the effect of such material in the cavities. Projected in this study is a series of experiments in an autoclave so designed that appreciable and maintainable oxygen pressures in a larger vapor space can be employed instead of the relatively variable and uncontrollable pressures obtainable with H_2O_2.

In connection with protective film stabilization, the immediate projected work is concerned with investigation of the mechanism by which the spinel film
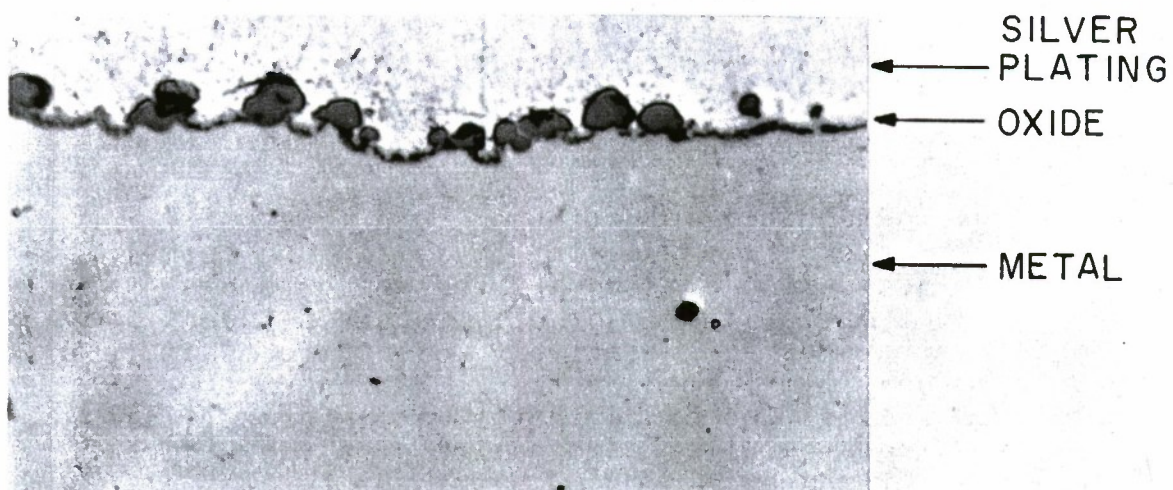
Fig. 18 - Spinel film formed on mild steel exposed to distilled water at 600°F for 6 weeks. Magnification: 1000X. (Reduction in printing approximately 6%.)
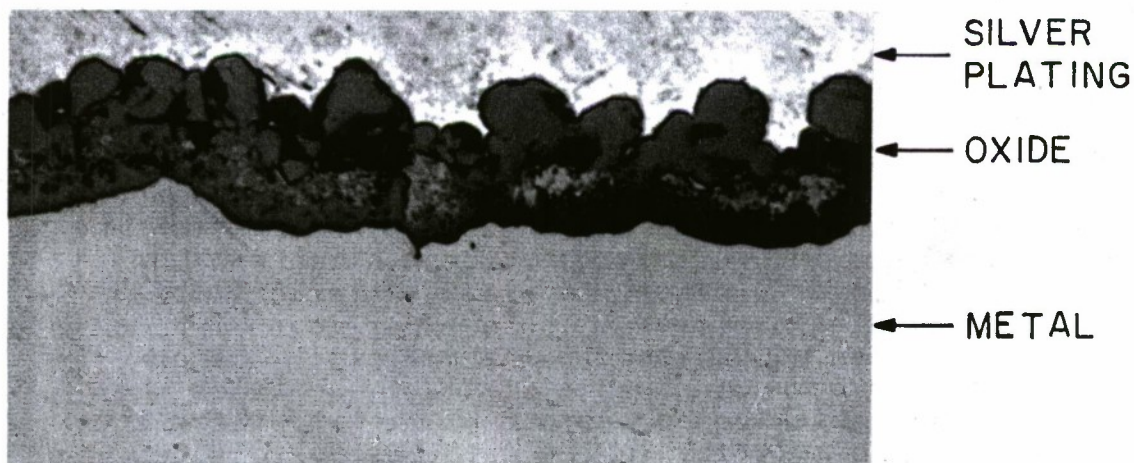

Fig. 19 - Spinel film formed on mild steel exposed to 0.1 molar LiOH at 600°F for 6 weeks. Magnification: 1000X. (Reduction in printing approximately 6%.)

stabilization is obtained in the case of the LiOH treatment. An initial series of experiments is scheduled in which the effects of large variations in the LiOH concentration and in 600°F exposure time will be investigated. Another series is planned using Li_2SO_4 solutions at the same varying molar concentrations as the Li^+ in the LiOH treatments above, and a third series in which analogous KOH solutions will be employed.

It is also planned that one or more of the specimens in each autoclave in subsequent experiments will be designed for use in electron microscopic examination along the lines of recent work done by Gulbransen (11) on oxidation films obtained at elevated temperature in the vapor phase. The data obtained in these studies will be used as guide lines for checking any conclusions reached in other cation substituent systems, as, for example, in $CuSO_4$ solutions, which have already, as indicated previously, shown some stabilization. The effect of other substituents in the solution or the metal will also be investigated.

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